Enclosed is a check for $475 for a three-month extension of time, paid as a small entity, to extend the time for response from May 25, 2004 to August 25, 2004. (37 C.F.R. § 1.136(a)(3)). If this amount is incorrect, please refer to the Deposit Account Authorization previously filed for this application. If any additional extension of time is required, please consider this paper a petition for the total extension of time required.

Reexamination and reconsideration of the application are respectfully requested.

Preliminary Note Concerning Ikenaga

A preliminary note: While reviewing the Office Action, the undersigned noted that the photocopy of the Ikenaga reference contained in the undersigned's file was of poor quality, and assumes that the copy previously submitted to the Office is of similar quality. The undersigned apologizes for any inconvenience. A better copy of this paper has now been obtained, and an additional copy is attached to this Reply as a courtesy. Because the Ikenaga paper has previously been properly cited, it is believed that the attached copy may be submitted in this informal manner, without the need for a new, formal IDC.

The Specification

The Office Action included certain comments of a general nature concerning the specification. Although a reply to this portion of the Office Action may not be strictly necessary, for the sake of completeness Applicant notes that there are no related copending applications, nor are there any "parent" applications from which priority is claimed.

The § 103 Rejections

All Claims were rejected under 35 U.S.C. § 103(a) as being obvious over one of three cited references. No other grounds of rejection were entered.

Claim 1 is the sole independent Claim. If an independent Claim is novel and nonobvious, it necessarily follows that its dependent Claims are likewise novel and nonobvious. For the sake of simplicity, the discussions below therefore focus on independent Claim 1 only. Applicant reserves the right to present alternative arguments concerning the dependent Claims in the future, should the need arise.

Hiyama

Claims 1 and 6-9 were rejected as being obvious under 35 U.S.C. § 103(a) over Hiyama.

For purposes relevant to the February 25, 2004 § 103 rejection, Hiyama appears to be cumulative to Ikenaga. It is therefore respectfully submitted that the Hiyama paper *per se* need not be further considered.

The Hiyama paper is a review article. The Office particularly cited page 422 of Hiyama. That page of Hiyama includes a reference to Hiyama's footnote 4, which in turn cites three papers, one of which is the Ikenaga paper cited in the February 25, 2004 Office Action. Note also that Reactions (4) on page 422 of Hiyama are essentially identical to Reactions (4) and (5) on page 1961 of Ikenaga.

At least for purposes relevant to the § 103 rejection, Hiyama appears to be cumulative to Ikenaga. It is therefore respectfully submitted that the § 103 analysis may

focus solely on Ikenaga, and that Hiyama need not be analyzed separately. For the reasons given below in the discussion of Ikenaga, it is respectfully submitted that the rejections over both Ikenaga and Hiyama should be withdrawn.

Strictly in the alternative, it is respectfully suggested that the Office should withdraw the rejection over Hiyama, even if the rejection over Ikenaga were maintained, since Hiyama is merely cumulative.

Ikenaga

Claims 1 and 6-9 were rejected as being obvious under 35 U.S.C. § 103(a) over Ikenaga.

Ikenaga neither teaches nor suggests the claimed invention.

Nothing in Ikenaga teaches or suggests a cross-coupling reaction between an aryldiazonium salt and an "arylsilane," as required by independent Claim 1. Rather, as explained below, Ikenaga teaches the different reaction of an aryldiazonium salt and an "alkenylsilane."

Nothing in Ikenaga would motivate one of ordinary skill in the art to modify the disclosed reactions of alkenylsilanes into reactions of arylsilanes. Nor, even assuming for the sake of argument that some such motivation had existed (and there was none), would there have been any reasonable expectation that such a modification would be successful.

Independent Claim 1 has limitations directed to reacting an "arylsilane" with an aryldiazonium salt, "wherein the arylsilane comprises Ar'-Si$(L)_3$; wherein Ar' is aryl . . . ."

A patent specification is, of course, interpreted as it would be understood by a person of ordinary skill in the art. A person of ordinary skill in the art, i.e., an experienced synthetic organic chemist, would understand the limitation to an "arylsilane" comprising "Ar'-Si$(L)_3$; wherein Ar' is aryl" to mean that the aromatic functionality Ar' is covalently bonded directly to the silicon atom. A person of ordinary skill in the art would not understand this limitation to include a compound that happens to have both a silane group and an aromatic group in different parts of the same molecule, if the two are not directly bonded to one another.

Synthetic organic chemists generally tend to describe a group of related compounds, compounds that might be substituted for one another in a particular synthesis, with language that is useful from a synthetic or mechanistic perspective, not language that is merely descriptive of different components of a molecule. Thus, an "arylsilane," in particular an arylsilane that "comprises Ar'-Si$(L)_3$; wherein Ar' is aryl," would be understood in this context to refer to a molecule in which the silane functionality is directly bonded to the aromatic functionality.

Further confirmation of this interpretation, if confirmation is needed, may be seen in the specification. For example: **(1)** Every example of an "arylsilane" given in the specification shows or describes a compound in which a phenyl ring is directly bonded to a silicon atom. None depict an aromatic functionality and a silane functionally that are found in separate parts of the same compound, but that are not directly bonded to one another. **(2)** The specification describes a proposed reaction mechanism in paragraph [0030], and illustrates it in Scheme 9 on page 14. Whether or not the proposed reaction

mechanism is correct may be disregarded for the moment. The important observation for the time being is the light that the proposed mechanism sheds on the proper interpretation of the term "arylsilane." The proposed electrophilic aromatic addition mechanism requires that the aromatic ring be directly bonded to the silyl group. The proposed mechanism would otherwise be inapplicable. Thus, regardless of whether a worker of ordinary skill in the art accepted the proposed mechanism, that mechanism would nevertheless confirm to the worker of ordinary skill in the art that the term "arylsilane" means a molecule in which a silane functionality is directly bonded to an aromatic functionality.

Ikenaga, by contrast, describes cross-coupling reactions of "alkenylsilanes," not "arylsilanes." The Ikenaga paper refers repeatedly to "alkenylsilanes," but never to "arylsilanes" - - notwithstanding the fact that phenyl substituents are present in several of Ikenaga's "alkenylsilanes." As previously discussed, synthetic organic chemists generally tend to describe a group of related compounds, compounds that might be substituted for one another in a particular synthesis, with language that is useful from a synthetic or mechanistic perspective, not language that is merely descriptive of different components of a molecule. Consistent with this general practice, Ikenaga's "alkenylsilanes" are all compounds in which an alkenyl group is covalently bonded directly to a silicon atom. Ikenaga never refers to the disclosed compounds as "arylsilanes," presumably because Ikenaga discloses no "arylsilanes," as that term would be understood by one of ordinary skill in the art. Ikenaga's general nomenclature is, however, entirely consistent with the naming conventions discussed here.

As another example, Ikenaga repeatedly refers to "arenediazonium salts" in referring to the structure ArN_2X. In these compounds an aromatic group is bonded directly to a diazonium group. Again, Ikenaga's nomenclature is consistent with the naming conventions discussed here.

Note also that the proposed reaction mechanisms of Ikenaga's Schemes 1, 2, and 3 on pages 1961 and 1962 focus on the alkenyl double bond, but do not directly depend on the aromatic nature of the phenyl substituent. (Ikenaga did report, however, that the electron-donating or -withdrawing characteristics of substituents on the aromatic ring appeared to affect the rate and yield of the reaction.) Ikenaga discloses reactions of alkenylsilanes, not reactions of arylsilanes.

Also note that the background section of the present specification expressly contrasts the prior Ikenaga-type reaction with the present invention. See paragraph [0011] and Scheme 6 on page 7 of the present specification, where the Ikenaga-type reaction cited by the February 25, 2004 Office Action is specifically included in Applicant's discussion of the prior art. By recognizing and including this reaction in the prior art discussion, the specification clearly contrasted the novel cross-coupling reactions of arylsilanes from prior art reactions with alkenylsilanes – including alkenylsilanes that, as expressly shown in Scheme 6 of the present specification, may in some cases have included aromatic substituents. The specification's explicit acknowledgment that the reaction of Scheme 6 lies within the prior art is a clear indication that "alkenylsilanes" are not considered to be "arylsilanes," even where an alkenylsilane might include an aromatic constituent. In interpreting a limitation in a claim as originally filed, it is only reasonable to

give the limitation an interpretation that would not cause the Claim to encompass something that the background section of the specification had expressly described as being within the prior art. This should be especially true where the interpretation that avoids the prior art is fully consistent with common usage in the field.

In view of the very different character of alkenyl double bonds and of aromatic ring structures, one of ordinary skill in the art would not, in general, have any motivation to modify reactions of the former into reactions of the latter. Furthermore, even if one assumed for the sake of argument that some such motivation had existed (and there was none), there still would have been no reasonable expectation of success. Ikenaga would not have made the claimed inventions obvious.

Ikenaga summary.

Ikenaga neither teaches nor suggests the reaction of independent Claim 1. It is respectfully submitted that the § 103 rejection over Ikenaga should be withdrawn.

Spivak

Claims 1-9 were rejected under 35 U.S.C. § 103(a) as being obvious over the Spivak *et al.* Poster and Abstract.

As the enclosed Affidavit of inventor David A. Spivak demonstrates, the Spivak *et al.* Poster and Abstract represent a publication of the inventor's own work. Because both were published less than one year before the filing date of the present application, the Spivak *et al.* Poster and Abstract have been removed as references.

Section 103 Summary

It is respectfully submitted that all prior art rejections have been overcome, or should otherwise be withdrawn.

Strictly in the alternative, if the Office agrees that the Spivak *et al.* Poster and Abstract have been removed as a reference, but the Office nevertheless maintains the rejection over Ikenaga, then it is respectfully submitted that the Office should acknowledge that at least Claims 2-5 are directed to allowable subject matter. The only rejection that was entered against Claims 2-5 was a rejection over the Spivak *et al.* Poster and Abstract. Thus, once the Poster and Abstract are removed as a reference, no rejections of Claims 2-5 will remain. If appropriate, Claims 2-5 might then still be objected to as depending from a rejected independent Claim, but Claims 2-5 should be acknowledged as otherwise being directed to allowable subject matter.

Further in the alternative, in the event that the Office should enter any new rejection of any of Claims 2-5, i.e., a rejection of any of Claims 2-5 for any reason other than a § 103 rejection over the Spivak Abstract and Poster, then it is respectfully submitted that the next Office Action should not be made final. The Office's attention is respectfully directed to M.P.E.P. § 706.07(a), which provides that second or subsequent actions should not be made final "where the examiner introduces a new ground of rejection that is neither necessitated by applicant's amendment of the claims nor based on information submitted in an information disclosure statement filed during the period set forth in 37 CFR 1.97(c) with the fee set forth in 37 CFR 1.17(p)." The Claims have not been amended, and no new

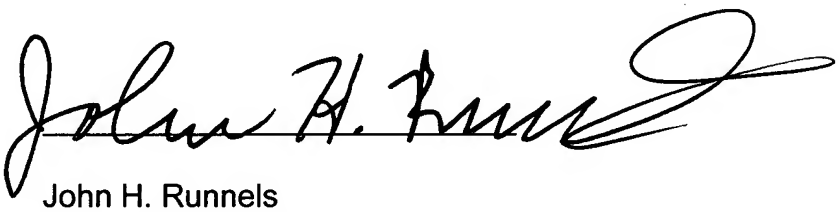
references have been submitted. It therefore follows that if any new ground of rejection should be entered against any of Claims 2-5, then the next action should not be final.

It is repeated that these arguments concerning Claims 2-5 are made strictly in the alternative, and that for the reasons given above all pending Claims should now be allowed.

Conclusion

Allowance of Claims 1-9 at an early date is respectfully requested.

Respectfully submitted,



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August 13, 2004

Reaction of Diazonium Salts with Transition Metals. Part 11.[1] Palladium-catalyzed Aryldesilylation of Alkenylsilanes by Arenediazonium Salts

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Under palladium(0) catalysis, both (*E*)- and (*Z*)-RCH=CHSiMe$_3$(R=Rh, 4-MeC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, n-C$_6$H$_{13}$, and MeOCH$_2$) were easily aryldesilylated by ArN$_2$X (Ar=Ph, 4-MeC$_6$H$_4$, 4-BrC$_6$H$_4$ and 4-NO$_2$C$_6$H$_4$; X=BF$_4$, PF$_6$, and Cl) to give (*E*)-RCH=CHAr and RC(Ar)=CH$_2$ as the main products at 25 °C in acetonitrile. *anti*- and *syn*-1,2-Elimination of Pd(0) and Me$_3$Si from the adducts, *threo*- and *erythro*-RCH(PdX)CHSiMe$_3$, generated from ArPdX and (*E*) and (*Z*)-RCH=CHSiMe$_3$, respectively, are proposed for the formation of (*E*)-RCH=CHAr from either isomer of RCH=CHSiMe$_3$.

Over the past ten years, alkenylsilanes have been increasingly used in organic synthesis as key intermediates. The reactivity of alkenylsilanes with a variety of electrophiles by regio- and stereospecific pathways is now well documented.[2] However, few transition metal-mediated reactions *via* alkenylsilanes have been reported because of the low reactivity of the Si–C bond towards transmetallation. Reactions of (*E*)-PhCH=CHSiMe$_3$ or (*E*)-PhCH=CHSiF$_5^-$ with palladium salts[2] have been described to form (*E*)-PhCH=CH–Pd–intermediates with retention of their geometry through an addition–elimination[3] or a transmetallation[4] mechanism. Unfortunately, the corresponding (*Z*)-isomers were not investigated in these reactions.

Palladium-catalyzed reactions of arenediazonium salts (ArN$_2$X) involve an arylpalladium species (ArPdX) as a key intermediate.[1,5–8] In a preliminary communication,[9] we reported that both (*E*)- and (*Z*)-PhCH=CHSiMe$_3$ were easily aryldesilylated by [ArPd]$^+$BF$_4^-$ generated from ArN$_2$BF$_4$ and bis(dibenzylideneacetone)palladium(0) [Pd(dba)$_2$] to give (*E*)-PhCH=CHAr and PhC(Ar)=CH$_2$, but not (*Z*)-PhCH=CHAr. The palladium-catalyzed reaction of CH$_2$=CHSiMe$_3$ with ArN$_2$BF$_4$ gave ArCH=CH$_2$, (*E*)-ArCH=CHSiMe$_3$ and ArC(SiMe$_3$)=CH$_2$.[10] We now wish to report the palladium-catalyzed reactions of (*E*)- and (*Z*)-RCH=CHSiMe$_3$(R=aryl and alkyl) with ArN$_2$X(X=BF$_4$, PF$_6$, and Cl), and their stereochemical features.

Results and Discussion

No appreciable reactions of the alkenylsilanes with ArN$_2$X could be observed in the absence of a palladium catalyst. The addition of Pd(dba)$_2$ (5 mol%) to a solution of (*E*)-PhCH=CHSiMe$_3$ [(*E*)-(**4a**)] and ArN$_2$BF$_4$ (**1a**—**d**) in acetonitrile at 25 °C caused a rapid gas evolution and gave a clear yellow solution. A g.c. analysis of the reaction mixture and n.m.r. analysis of the isolated products showed the formation of (*E*)-PhCH=CHAr[(*E*)-(**5a**—**d**)] and PhC(Ar)=CH$_2$(**6a**—**d**) [Equation (1)]. The results are summarized in Tables 1 and 2.

$$\underset{\substack{(E)\text{-}(\mathbf{4a})\\(Z)\text{-}(\mathbf{4a})}}{\text{PhCH=CH} \sim \text{SiMe}_3} + \text{ArN}_2\text{X} \xrightarrow[\substack{(\mathbf{1a}\text{—}\mathbf{d})\text{X=BF}_4\\(\mathbf{2a,c})\text{X=PF}_6\\(\mathbf{3c})\text{X=Cl}}]{\text{Pd(dba)}_2\text{–CH}_3\text{CN, 25 °C}} \underset{(\mathbf{5a}\text{—}\mathbf{d})}{\text{PhCH=CH} \sim \text{Ar}} + \underset{(\mathbf{6a}\text{—}\mathbf{d})}{\text{PhC(Ar)=CH}_2} \quad (1)$$

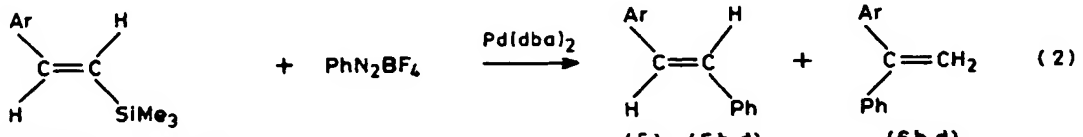
a; Ar=Ph, **b**; Ar=4-MeC$_6$H$_4$, **c**; Ar=4-BrC$_6$H$_4$, **d**; Ar=4-NO$_2$C$_6$H$_4$

More than a trace of (*Z*)-(**5**) could not be detected in all the reactions with (**1a**—**d**). Both electron-donating and -withdrawing groups on (**1**) could be used successfully and the arylated styrenes were obtained in quantitative yields in the reactions with (*E*)-(**4a**), although the electron-withdrawing groups reduced the rates considerably and increased the isomer ratio, (**5**):(**6**).

Entries 4 and 5 in Table 1 show the effects of substituents on the aromatic ring of compound (*E*)-(**4**) in the reaction with (**1a**) [Equation (2)]. The rate in this case was more sensitive to the presence of both electron-donating and -withdrawing groups on compound (**4**) as compared to those on compound (**1**).

The reactions with (*Z*)-(**4a**) required more than 10 mol% of Pd(dba)$_2$ to obtain reasonable yields and rates. Unexpectedly compound (*Z*)-(**5**) was not observed in the arylated products. Neither of starting alkenylsilanes (*E*)- and (*Z*)-(**4a**), isomerized during the reactions, although very slow isomerization of (*Z*)-(**4a**) to (*E*)-(**4a**) was observed when the reaction mixture was allowed to stand for a few days at room temperature. A control reaction of compound (**1b**) with (*E*)- or (*Z*)-(**4a**) in the presence of (*E*)- and (*Z*)-(**5a**) clearly showed that no isomerization occurred in either product isomer, (*E*)- and (*Z*)-(**5a**), under these particular reaction conditions. In the reaction with (*Z*)-(**4a**), the electron-withdrawing groups on compound (**1**) did not decrease the rates but rather accelerated them.

The effects of the counter anion of ArN$_2$X are summarized in Table 3. ArN$_2$PF$_6$ (**2**) also could be favourably used in the



(*E*)-(**4b**)(Ar = 4 - MeC$_6$H$_4$)
(*E*)-(**4d**)(Ar = 4 - NO$_2$C$_6$H$_4$)
(*E*)-(**5b,d**)
(**6b,d**)
(2)

Table 1. Palladium-catalyzed aryldesilylation of (*E*)-ArCH=CHSiMe$_3$[(*E*)-(**4a—d**)] by ArN$_2$BF$_4$ (**1a—d**) [Equations (1) and (2)]

Entry	Ar in ArHC=CHSiMe$_3$	Ar in ArN$_2$BF$_4$	Pd(dba)$_2$ (mol %)	Rates[a] (% min^{-1})	Yields[b] (%)	Products (% ratio)[c] PhHC=CHAr	Ph(Ar)C=CH$_2$
1	Ph[(*E*)-(**4a**)]	Ph(**1a**)	2	4.1	81	(*E*)-(**5a**) (76)	(**6a**) (24)
2	(*E*)-(**4a**)	(**1a**)	5	13	98	(*E*)-(**5a**) (67)	(**6a**) (33)
3	(*E*)-(**4a**)	(**1a**)	20	47	99	(*E*)-(**5a**) (57)	(**6a**) (43)
4	4-Me-C$_6$H$_4$-[(*E*)-(**4b**)]	(**1a**)	5	22	100	(*E*)-(**5b**) (74)	(**6b**) (26)
5	4-NO$_2$-C$_6$H$_4$-[(*E*)-**4d**)]	(**1a**)	5	0.31	67	(*E*)-(**5d**) (65)	(**6d**) (35)
6	(*E*)-(**4a**)	4-Me-C$_6$H$_4$-(**1b**)	5	16	97	(*E*)-(**5b**) (58)	(**6b**) (42)
7	(*E*)-(**4a**)	4-Br-C$_6$H$_4$-(**1c**)	5	9.4	100	(*E*)-(**5c**) (65)	(**6c**) (35)
8	(*E*)-(**4a**)	4-NO$_2$-C$_6$H$_4$-(**1d**)	5	4.6	99	(*E*)-(**5d**) (86)	(**6d**) (14)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on the amount of compound (**1**) used. [c] Determined by g.c.

Table 2. Palladium-catalyzed aryldesilylation of (*Z*)-PhCH=CHSiMe$_3$[(*Z*)-(**4a**)] by ArN$_2$BF$_4$ (**1a—d**) [Equation (1)]

Entry	Ar in ArN$_2$BF$_4$	Pd(dba)$_2$ (mol %)	Rate[a] (% min^{-1})	Yield[b] (%)	Products (% ratio)[c] PhHC=CHAr	Ph(Ar)C=CH$_2$
9	Ph-(**1a**)	5	3.0	14	(*E*)-(**5a**) (76)	(**6a**) (24)
10	(**1a**)	10	7.7	97	(*E*)-(**5a**) (80)	(**6a**) (20)
11	(**1a**)	20	30	100	(*E*)-(**5a**) (74)	(**6a**) (26)
12	4-MeC$_6$H$_4$-(**1b**)	5	3.1	54	(*E*)-(**5b**) (74)	(**6b**) (26)
13	(**1b**)	10	5.2	68	(*E*)-(**5b**) (70)	(**6b**) (30)
14	4-BrC$_6$H$_4$-(**1c**)	5	4.3	45	(*E*)-(**5c**) (64)	(**6c**) (36)
15	(**1c**)	10	6.0	100	(*E*)-(**5c**) (76)	(**6c**) (24)
16	4-NO$_2$C$_6$H$_4$(**1d**)	5	6.4	77	(*E*)-(**5d**) (75)	(**6d**) (25)
17	(**1d**)	10	8.2	84	(*E*)-(**5d**) (76)	(**6d**) (24)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on the amount of compound on (**1**) used. [c] Determined by g.c.

Table 3. Effects of counter anion of ArN$_2$X(**1—3**) on palladium-catalyzed aryldesilylation of (*E*)- and (*Z*)-PhCH=CHSiMe$_3$(**4a**) by ArN$_2$X [Equation (1)]

Entry	(*E*) or (*Z*) (**4a**)	ArN$_2$X Ar; X	Pd(dba)$_2$ (mol %)	Rates[a] (% min^{-1})	Yields[b] (%)	Products (% ratio)[c] HPhC=CHAr	HPhC=CHAr	Ph(Ar)C=CH$_2$
1	(*E*)	Ph; BF$_4$ (**1a**)	5	13	98	(*E*)-(**5a**) (67)		(**6a**) (33)
18	(*E*)	Ph; PF$_6$ (**2a**)	5	28	86	(*E*)-(**5a**) (85)		(**6a**) (15)
7	(*E*)	4-BrC$_6$H$_4$; BF$_4$ (**1c**)	5	9.4	100	(*E*)-(**5c**) (65)		(**6c**) (35)
19	(*E*)	4-BrC$_6$H$_4$PF$_6$ (**2c**)	5	10	100	(*E*)-(**5c**) (86)		(**6c**) (14)
20	(*E*)	4-BrC$_6$H$_4$; Cl (**3c**)	5	4.3	14	(*E*)-(**5c**) (94)	(*Z*)-(**5c**) (6)	(**6c**) (trace)
21	(*E*)	(**3c**)	20		37	(*E*)-(**5c**) (95)	(*Z*)-(**5c**) (5)	(**6c**) (trace)
14	(*Z*)	(**1c**)	5	4.3	45	(*E*)-(**5c**) (64)		(**6c**) (36)
22	(*Z*)	(**2c**)	5		100	(*E*)-(**5c**) (86)		(**6c**) (14)
23	(*Z*)	(**3c**)	18		22	(*E*)-(**5c**) (90)	(*Z*)-(**5c**) (7)	(**6c**) (3)

[a] Steady state rates at early stage estimated by the gas evolution. [b] g.c. yields based on ArN$_2$X used. [c] Determined by g.c.

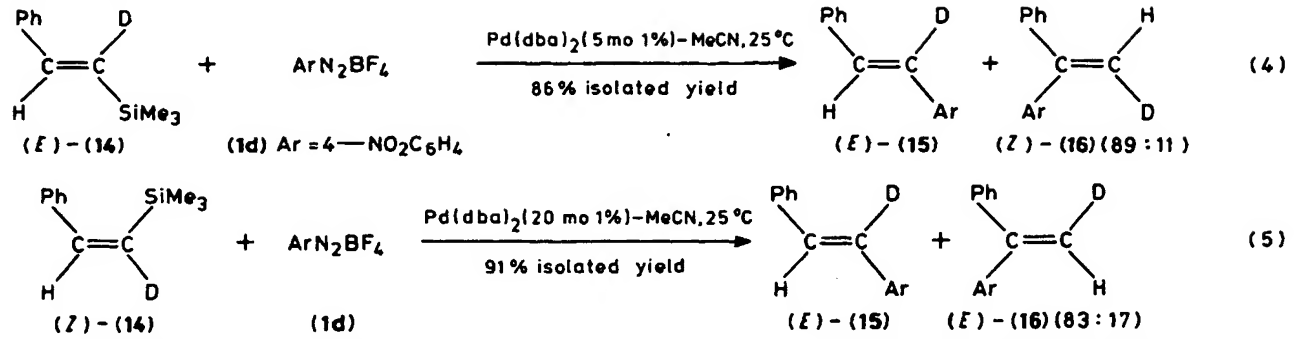
Table 4. Palladium-catalyzed reactions of n-C$_6$H$_{13}$CH=CHSiMe$_3$(**7a**) and MeOCH$_2$CH=CHSIMe$_3$ (**7b**) with PhN$_2$BF$_4$ (**1a**) [Equation (3)]

Entry	Silane	Pd(dba)$_2$ (mol %)	Yield[a] (%)	Products, % ratio[b] (**8**)	(**9**)	(**10**)	(**11**)	(**12**) (*E*/*Z*)	(**13**) (*E*/*Z*)	Unknown
24	(*E*)-(**7a**)	3	76	18	11	39	21	6(0/100)	2(100/0)	3
25	(*Z*)-(**7a**)	5	71	17	17	36	17	9(78/22)	5(60/40)	10
26	(*E*)-(**7b**)	5	(23)[c]	0	0	66	16	5		13[d]
27	(*Z*)-(**7b**)	20	(13)[c]	0	0	56	41	Trace		3[d]

[a] Unless otherwise noted g.c. yields based on (**1a**). [b] Determined by g.c. [c] Isolated yields based on the amount of compound (**1a**) used. [d] PhCH=CHCHO was present.

$$\begin{aligned} \text{RCH=CH} \sim \text{SiMe}_3 + \text{PhN}_2\text{BF}_4 \xrightarrow{\text{Pd(dba)}_2\text{-MeCN, 25 °C}} & \quad (E)\text{-RCH=CHPh} + \text{R'CH=CH} \sim \text{CH}_2\text{Ph} \\ (E)\text{-(7a,b)} \quad (Z)\text{-(7a,b)} & \quad (\mathbf{8a,b}) \quad (\mathbf{9a,b}) \\ & + \text{RC(Ph)=CH}_2 + \text{R'} \sim \text{CH=C(Ph)Me} \\ & \quad (\mathbf{10a,b}) \quad (\mathbf{11a,b}) \\ & + \text{R} \sim \text{CH=C(Ph)SiMe}_3 + \text{RC(Ph)=CH} \sim \text{SiMe}_3 \\ & \quad (\mathbf{12a,b}) \quad (\mathbf{13a,b}) \end{aligned} \qquad (3)$$

a; R=n-C$_6$H$_{13}$, R'=n-C$_5$H$_{11}$, **b**; R=MeOCH$_2$, R'=MeO

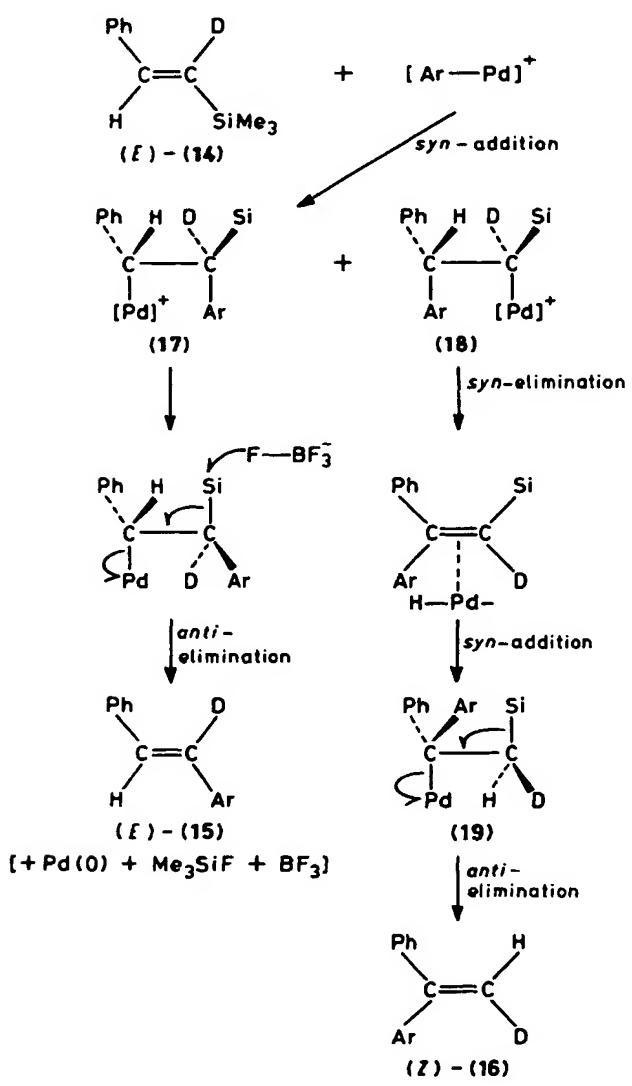


present aryldesilylation with an increase in the rate. In contrast to compound (**1c**), the reaction of (*Z*)-(**4a**) with compound (**2c**) gave a quantitative yield of arylated styrenes in the presence of only 5 mol% of $Pd(dba)_2$.

It was difficult to obtain pure and anhydrous crystals of ArN_2Cl (**3**),[11] except for 4-$BrC_6H_4N_2Cl$ (**3c**) in the present study. The use of compound (**3c**) drastically depressed the yields and regioselectively gave the product (**5c**). Interestingly, (*Z*)-(**5c**) was formed with either isomer (*E*)- or (*Z*)-(**4a**), although the yields were still very low and (*E*)-(**5c**) was the principal product. The extremely low yield in entry 23 in spite of its moderate rate suggested catalyst decay during the reaction. The decomposition products from (**3c**), which are well known to be unstable in anhydrous form, might deactivate the catalyst.

In the presence of a palladium(0) catalyst,[12] (*E*)- and (*Z*)-n-$C_6H_{13}CH{=}CHSiMe_3$[(*E*)- and (*Z*)-(**7a**)], and (*E*)- and (*Z*)-$MeOCH_2CH{=}CHSiMe_3$[(*E*)-and (*Z*)-(**7b**)] also reacted easily with compound (**1a**) to give the phenyldesilylated products (**8**)—(**11**) along with small amounts of the phenylated alkenylsilanes (**12**) and (**13**) [Equation (3) and Table 4]. The presence of allylic hydrogen may account for the formation of the isomerized products, (**9**) and (**11**). When the reactions of compound (**7a**) were conducted in moist acetonitrile or without exclusion of atmospheric moisture, at least 8 isomers of phenyloctene were obtained. It is possible that a protic acid, such as HBF_4, generated under moist conditions might promote the isomerization of both starting silanes and phenylated products.

Reactions of deuteriated styryltrimethylsilanes [(*E*)- and (*Z*)-(**14**)] with compound (**1d**) were employed to clarify the stereochemistry of the present aryldesilylation. Both isomers gave the same deuteriated nitrostilbene, (*E*)-(**15**), as the major product. Whereas the minor product, (*Z*)- or (*E*)-deuteriated nitrodiphenylethylene [(*Z*)- or (*E*)-(**16**)] was obtained stereospecifically from (*E*)- or (*Z*)-(**14**), respectively [Equations (4) and (5)].

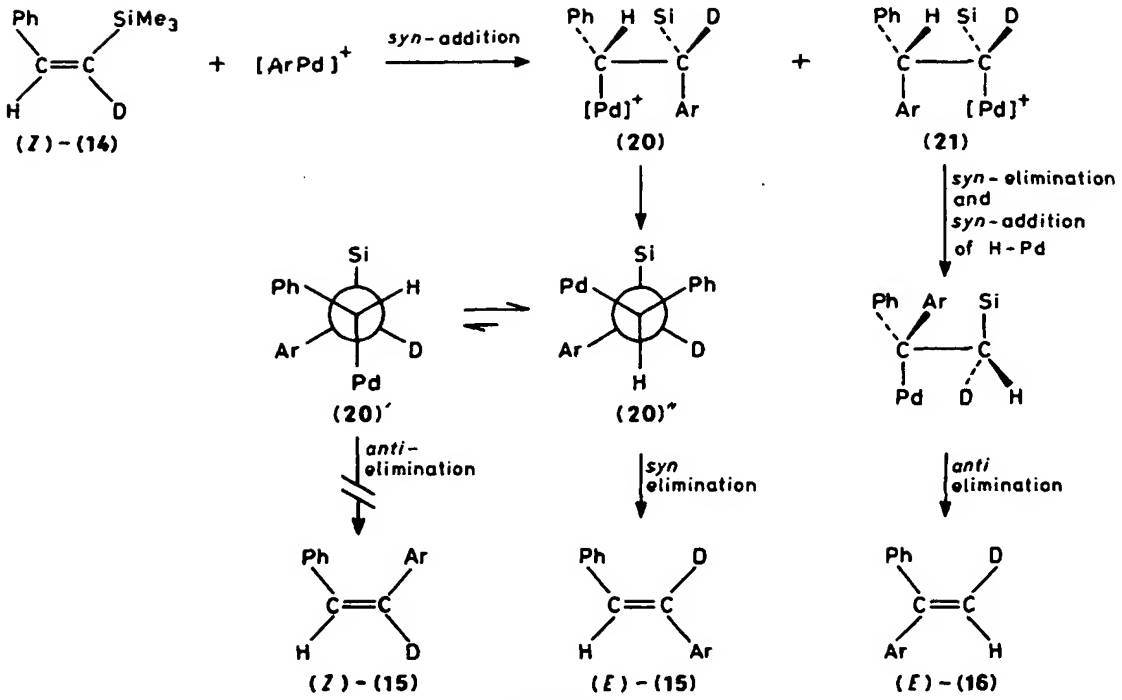


Scheme 1.

Mechanism.—Some reactions of organosilicon compounds with palladium complexes have been described as proceeding *via* a transmetallation mechanism.[4,13] However, the loss of regioselectivity in the present reaction system seems to be more compatible with an addition–elimination mechanism rather than transmetallation. Since ArPdX is known to add easily to alkenes at ambient temperature with *syn*-stereochemistry,[5,14,15] the addition of $[ArPd]^+BF_4^-$ generated from compound (**1**) and zero-valent palladium to alkenylsilanes can be reasonably expected as an initial step in the present aryldesilylation as shown in Schemes 1 and 2. The orientation of the addition to give compounds (**17**) and (**18**) [or (**20**) and (**21**)] determines the regiochemistry. *anti*-Elimination of Pd(0) and Me_3Si moieties from (**17**) gives compound (*E*)-(**15**). Such an *anti*-elimination is the most common process for organosilicons in which there is a leaving group at the β-position.[16] Zero-valent palladium is also well known to be a good leaving group in the reaction of π-allylic palladium compounds with nucleophiles.[17]

In the adducts (**18**) and (**21**) palladium should be transposed with the neighbouring carbon to undergo desilylation. The stereospecific formation of (*Z*)-(**16**) from (*E*)-(**14**), and of (*E*)-(**16**) from (Z)-(**14**) can be reasonably interpreted by supposing that the isomerization of compounds (**18**) and (**21**), respectively, proceeds *via syn*-elimination and re-addition of an H–Pd species followed by *anti*-elimination of Pd(0) and Me_3Si moieties as shown in Schemes 1 and 2.

The formation of the phenylated trimethylsilylalkenes (**12**) and (**13**) from compound (**7**) may be related to the high co-



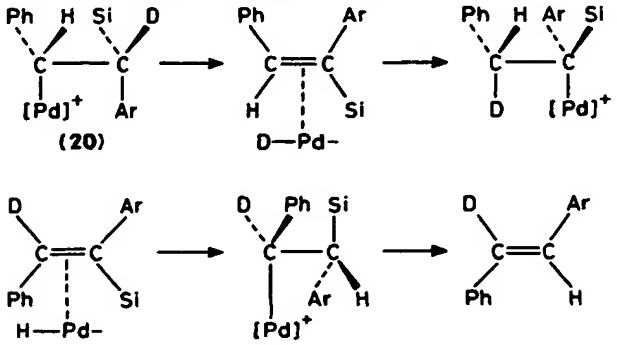
Scheme 2.

ordinating ability of (7) to an H-Pd species [Equations (6) and (7)].[10,12]

$$RCH(Ph)-CH(Pd)-SiMe_3 \rightleftharpoons RC(Ph)(H\text{-}Pd)=CH-SiMe_3 \quad (6)$$

$$RC(Ph)(H\text{-}Pd)=CHSiMe_3 + RCH=CHSiMe_3 \rightleftharpoons RC(Ph)=CHSiMe_3 + RCH(H\text{-}Pd)=CHSiMe_3 \quad (7)$$

In the reactions of the (*E*)-isomers, the moderate rate retardation by the presence of a 4-nitro group on compound (**1**) and the drastic reduction caused by the same substituent on compound (*E*)-(**4d**) suggested that the important step is the elimination of Pd(0) from the initial adduct (**17**) *via* an *E*1-like pathway. The *E*1-like pathway is reasonable because the β-effect[18] of the silicon atom (stabilization of β-carbenium ions) is supposed to be an important factor in the *anti*-elimination of β-heteroatom-substituted organosilicons.[16]



Scheme 3.

In the reaction of (*Z*)-isomers (*Z*)-(**4a**) and (*Z*)-(**14**), the same *anti*-elimination of Pd(0) and Me_3Si moieties from the initial adducts, such as (**20**) in Scheme 2, cannot explain the formation of the products (*E*)-(**5**) and (*E*)-(**15**). One of the possible pathways for the unexpected stereochemistry is an isomerization of the intermediate adduct (**20**) *via* elimination and addition of DPd (or HPd) species as shown in Scheme 3. Since *syn*-stereochemistry of the elimination and addition of H–Pd is well documented, the isomerization process inevitably transposes deuterium from the α- to the β-carbon, and produces (*E*)-PhCD=CHAr. However, the n.m.r. spectrum of the (*E*)-stilbene derivatives from (*Z*)-(**14**) was the same as that from (*E*)-(**14**). The oxidative cleavage of (*E*)-(**4d**) by $NaIO_4$–OsO_4[19] gave 4-$NO_2C_6H_4CHO$ and PhCHO with aldehyde proton resonances at 10.03 and 9.90 p.p.m., respectively, in the n.m.r. spectra. The n.m.r. spectra of the similar oxidation products of (*E*)-stilbene derivatives obtained from compound (*Z*)-(**14**) showed only one resonance at 9.90 p.p.m. in aldehyde proton region. Thus, it was concluded that the product from (*Z*)-**14**) was (*E*)-(**15**).

syn-Elimination of Pd(0) and Me_3Si moieties from the intermediate (**20**) can reasonably explain the formation of compound (*E*)-(**5**) from (*Z*)-(**4a**) and of (*E*)-(**15**) from (*Z*)-(**14**). In this case, an *anti*-elimination requires the more sterically congested conformer (**20**)′. Thus the elimination would take the *syn*-route *via* the more preferable conformer (**20**)″. R. B. Miller and G. McGarvey have reported that the mode of elimination of Me_3SiX (X=Br, Cl) from $Bu^tCH(X)CH(X)SiMe_3$ depends on the stability of the conformer.[20]

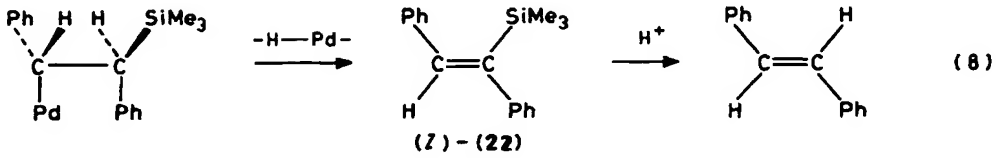
The contrasting effects of the substituents on compound (**1**) in the reactions with (*E*)- and (*Z*)-(**4a**) may reflect the different elimination pathways.[21]

For the present aryldesilylation, a combination of an elimination of HPdX from the initial adduct and a protodesilylation of the resulting alkenylsilane may be a possible alternative pathway [Equation (8)]. However, arylated styrylsilanes such as (*Z*)-(**22**) were not detected during the reaction. The control reactions shown in Table 5 revealed that the protodesilylation of (*E*)- and (*Z*)-PhCH=C(Ph)$SiMe_3$ were very slow, and gave stereospecifically compound (*Z*)- and (*E*)-(**5a**), respectively, although considerable isomerization was observed with increased reaction time. Consequently, the two-step mechanism could not be considered as a principal pathway in the present aryldesilylation.

Table 5. Protodesilylation of (*E*)- and (*Z*)-PhCH=CHSiMe$_3$[(*E*)- and (*Z*)-(**22**)] by HBF_4[a]

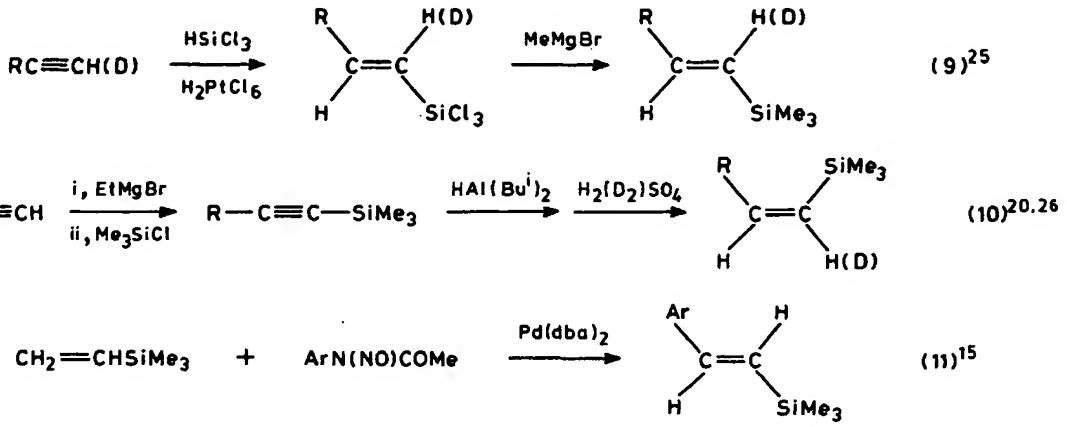
Entry	Silane (mmol)	HBF_4 (mmol)	Reaction time (min)	Conversion[b] (%)	Products, % yields[c] (*E*)-Stilbene	(*Z*)-Stilbene
28	HPhC≡CPhSiMe$_3$ (0.02)	0.019	25	5	4	0
		0.10	122	35	28	0.3
29	HPhC≡CPhSiMe$_3$ (0.02)	0.019	22	9	0.8	8
		0.14	124	48	11	35

[a] Reactions were started by the addition of 42% HBF_4 to a solution of a silylated diphenylethylene in acetonitrile (0.2 ml) at 25 °C. [b] Determined by g.c. [c] g.c. yields based on the alkenylsilanes used.



Experimental

Materials.—Acetonitrile was distilled from phosphorus pentaoxide (twice) and calcium hydride under nitrogen. Liquid arylamines were distilled before use. Guaranteed reagents of crystalline arylamines were used as received. ArN_2BF_4 (**1**),[22] ArN_2PF_6 (**2**),[23] and ArN_2Cl (**3**)[11] were prepared by the usual methods and stored under nitrogen at −20 °C. $Pd(dba)_2$ was prepared by the published method.[24] Alkenylsilanes were prepared by the following methods [Equations (9), (10), and (11)]. Their structure and purity were confirmed by n.m.r. and i.r. spectroscopy, and g.c. analysis (silicone SE-30 with FID). Isomeric purity estimated by g.c. of these alkenylsilanes was ≥99.9% except for (*Z*)-(**4a**) (96.0%) and (*E*)-(**7b**) (99.5%). The deuterium content of (*E*)- and (*Z*)-(**14**) estimated by n.m.r. spectroscopy was 86 and 97%, respectively. Compounds (*E*)- and (*Z*)-(**25**) were obtained by phenylation of (*E*)- and (*Z*)-(**4a**) with the $Pd(OAc)_2$–PPh_3 system,[15,27] respectively. Compound (*E*)-(**25**) was also prepared from PhC≡CPh by the hydrosilylation–methylation method described in Equation (9).



Aryldesilylation: General Procedure.—The reactions were started by the addition of $Pd(dba)_2$ to a solution of ArN_2X (0.5 mmol), an alkenylsilane (1.0 mmol), dioctyl ether (internal standard) and acetonitrile (5 ml) in a thermostatted cell (25.0 °C) equipped with a side arm and a septum cap. Gas evolution was measured by a gas burette connected to the side arm. Samples were withdrawn at appropriate time intervals by a micro-syringe and directly analyzed on g.c. with FID. After completion of the reaction, diethyl ether (50 ml) was added. The mixture was washed with aqueous sodium carbonate and brine, and dried (anhydrous $MgSO_4$). After removal of solvents, the residue was chromatographed on silica gel (eluting with hexane or hexane–diethyl ether).

The structure of arylated products was determined by comparison of their n.m.r. spectra and retention times on g.c. with those of authentic samples.[28] The resonances corresponding to *cis*- CH=CH could not be observed except for entries 20, 21, and 23 (Table 3). The formation of compound (*Z*)-(**6c**) was confirmed by comparison of its n.m.r. spectra and g.c. retention times with those of an authentic sample obtained by photochemical isomerization of compound (*E*)-(**5c**).[29] The structures of compounds (**8a**)—(**11a**) were determined by comparison of their g.c. retention times with those of authentic samples prepared by the reaction of oct-1-ene with the $Pd(OAc)_2$–PPh_3 system.[27] The structures of compounds (**10b**) and (**11b**) were assigned from their n.m.r. spectra: $Me^aOCH_2{}^bC(Ph)=CH_2{}^{c,d}$(**10b**), (p.p.m.), 3.39 (s, H^a), 4.32 (dd, H^b), 5.32 [dt, H^c (*Z*)], 5.50 [dt, H^d (*E*)], (J_{cd} 1.7, J_{bc} 1.7, J_{bd} 0.7 Hz); $Me^aOCH^b=C(Ph)Me^c$ (**11b**), 1.90 (s, H^c), 3.83 s, H^a), H^b was obscured by the signal due to the phenyl protons. The formation of compounds (**12a,b**) and (**13a,b**) was assumed by the comparison of the g.c. retention times of the reaction

mixture components with those of the products obtained from the reactions of (*E*)- and (*Z*)-(**7a,b**) with PhPdOAc.[15]

Reactions of (E)- *and* (Z)-$PhCH{=}CDSiMe_3$ *with* 4-$NO_2C_6H_4N_2BF_4$.—The same procedure as that described above was employed with compound (*E*)-(**14**) (2.0 mmol), (**1d**) (1 mmol), $Pd(dba)_2$ (0.05 mmol), and acetonitrile (10 ml), or with (*Z*)-(**14**) (1.0 mmol), (**1d**) (0.5 mmol) $Pd(dba)_2$ (0.1 mmol), and acetonitrile (5 ml). The ordinary work-up gave an isolated yield of 86% of arylated styrenes from (*E*)-(**14**) and 91% from (*Z*)-(**14**). The isomers were separated by medium pressure chromatography (Fuji-Gel CQ-3 with CCl_4–$CHCl_3$ as the eluant) with u.v. detection.

The stereochemistry of the deuteriated products was confirmed by the n.m.r. spectra of their epoxides which were prepared by the reaction with perbenzoic acid in chloroform. In the following structures, Ar refers to 4-$NO_2C_6H_4$: (*E*)-$PhCH^a{-}CH^bOAr$ [from (*E*)-(**5d**)] δ 3.84 (d, H^a), 3.94 (d, H^b). (J_{ab} 2.64 Hz); (*E*)-$PhCH^a{-}CODAr$ [from (*E*)-(**15**)] δ 3.83 (br s, H^a); $Ph(Ar)C{=}CH_2$ (**6d**), δ 5.48 [d, H^a (*E*)], 5.51 [d, H^b (*Z*)]. (J_{ab} 0.93 Hz); (*Z*)-$Ph(Ar)C{=}CH^aD$ [(*Z*)-(**16**)] δ 5.49 (br s, H^a); (*E*)-$Ph(Ar)C{=}CDH^b$ δ 5.51 (br s, H^b).

Reactions of (E)- *and* (Z)-$PhCH{=}CHSiMe_3$ *with* 4-Me-PhN_2BF_4 *in the presence of* (E)- *and* (Z)-PhCH=CHPh.—The reaction was started by the addition of $Pd(dba)_2$ (0.025 mmol) to a solution of compound (*E*)-(**4a**) (1.0 mmol) (**1b**) (0.5 mmol) dioctyl ether and acetonitrile (5 ml) in the presence of compound (**5a**) (0.14 mmol) (*E*:*Z* = 40:60) at 25 °C. The same procedure was employed in the reaction of compound (*Z*)-(**4a**) except for the use of $Pd(bda)_2$ (0.05 mmol) and (**5a**) (*E*:*Z* = 20:80) (0.60 mmol). The isomer ratio of compounds (**5a**) and the formation of (*E*)-(**5b**) and (**6b**) were monitored by g.c. In both cases the isomer ratios did not vary during the course of the reaction.

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